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(54) METHOD OF PRODUCING N-(2-PHENYL-VINYL) AMINOMALONIC ACID DIESTERS

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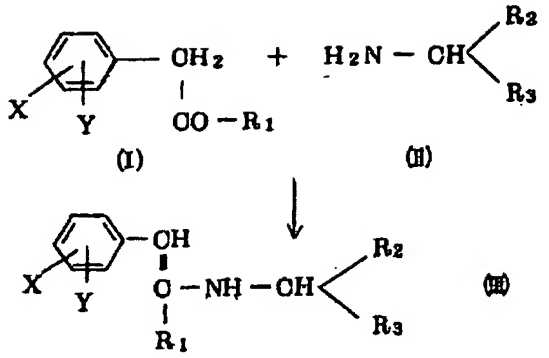
Detailed description of the invention

The present invention relates to a method of producing N-(2-phenyl-vinyl) aminomalonic acid diesters by reacting phenyl pyruvic acid (I) or salts thereof with aminomalonic acid diesters (II) or salts thereof to obtain N-(2-phenyl-vinyl)aminomalonic acid diesters (III).

The reactions concerning the present invention are represented by the formulas:



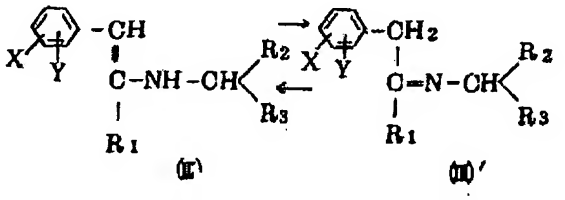
(wherein X is a halogen or a nitro group, Y is hydrogen, a halogen, or a nitro group, and R1, R2 and R3 are each independently the same or different and are an esterified carboxyl group.)

Of the starting materials (I), (2-nitro-3-chloro phenyl) pyruvic acid, for example, is produced by the methods set forth in the *Chemical Abstracts* Vol. 50, Paragraph 8598 i, by esterification of (2-nitro-chloro phenyl) pyruvic acid. Other starting materials are produced in a similar manner.

The compounds of the present invention is obtained by reacting the starting materials (I) or salts thereof with aminomalonic acid diesters (II) or salts thereof. The starting materials (I) are esters of phenyl pyruvic acid of which benzene ring is substituted at an arbitrary position by one or two groups selected from halogens such as chloride, bromine, iodine or fluoride or from nitro groups, , exemplary of such esters are alkyl esters such as methyl ester, ethyl ester, propyl ester, butylester and tertiary-butyl ester, or aralkyl esters such as benzyl ester and phenethyl ester, and the salts thereof are formed by the starting materials (I) with metals such as sodium, potassium and copper. The *aminomalonic acid diesters (II) are esters of aminomalonic acid, exemplary of* which are dialkyl esters such as dimethyl ester, diethyl ester, methyl-ethyl-ester, dipropyl ester, dibutyl ester and di-tertiary-butyl ester, or diaralkyl esters such as di-benzyl ester and diphenetyl ester, and the salts thereof are formed by the aminomalonic acid diesters (II) with mineral acids such as hydrochloric acid and sulfuric acid, or with organic acids such as acetic acid and propionic acid. The reaction is carried out with or without a solvent, and is also possible to add a base such as sodium acetate, piperidine, piperazine, pyridine, or trialkyl-amin. In *a case in which the salts of the aminomalonic acid diesters (II) are used for the* reaction, adding such bases is preferable. In a case in which a solvent is used for the reaction, for example, benzene-xylene, lower alcohols, dichloromethane, chloroform, tetrachloromethane, 1,2-dichloroethan, glacial acetic acid, or acetic acid is used according to the type of reaction. Additionally, in performing the reaction, a better result is often obtained when water formed in the reaction is removed as the reaction progresses.

The temperature of the reaction mixture is not restricted in particular but is determined based on the conditions such as the type of starting materials, whether or not a catalyst is used, or the type of solvents, and so forth. The reaction is often performed under the room temperature or at a heated temperature approximately of the boiling point of the solvent.

The target material (III) obtained by the present invention is a new material which is useful as intermediates for producing 3- phenylpyrroles having antibacterial action, for example. The target material (III) can be represented as tautomers (III') thereof of the formulas:



An example of the present invention is hereinafter described:

Example 1

7.0g of (2-nitro-3-chloro phenyl) pyruvate ethyl ester is heated to reflux for 24 hours with 5.0g of aminomaloriic acid diester, 117 anhydrous benzene, and two drops of glacial acetic acid. (As the reaction progresses, water formed in the reaction is distilled away from time to time as an azeotrope of water/benzene.) After the reaction has been completed, the reaction mixture is condensed and dried under reduced pressure to yield 11.0g of an oily, slightly dark brown product, N-{1- ethoxycarbonyl-2-(2-nitro-3-chloro phenyl) vinyl} aminomalonic acid diethyl ester.

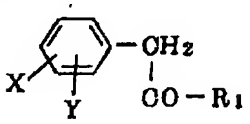
The resulting product has been observed in a following manner: The resulting product is heated with sodium hydride in anhydrous benzene under nitrogen gas stream, and 3-(2-nitro-3 chloro phenyl) - 4-hydroxy pyrrole-2, 5-dicarboxylate diethyl ester with mp154 -155 °C can be obtained.

Element analysis: $C_{16}H_{15}O_7N_2Cl$
Calculated value: O 50.20, H 3.96, N 7.32, Cl 9.26
Experimental value: O 50.03, H 3.88, N 7.39, Cl 9.28

Claim

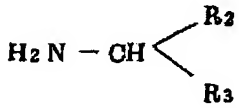
1. A method of producing N-(2-phenyl-vinyl) aminomalonic acid diesters to obtain N-(2-phenyl-vinyl) aminomalonic acid diesters,

wherein phenyl pyruvic acids or salts thereof of the formula:



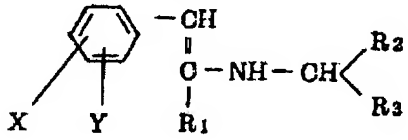
(wherein X is a halogen or a nitro group, Y is hydrogen, a halogen or a nitro group, R1 is an esterified carboxyl group.)

is reacted with aminomalonic acid diesters or salts thereof of the formula:



(wherein R2 and R3 are each independently the same or different and are an esterified carboxyl group.)

to obtain N-(2-phenyl-vinyl) aminomalonic acid diesters of the formula:



(wherein X, Y, R1, R2 and R3 are as previously described.)